

## Complex Materials Scattering (CMS)

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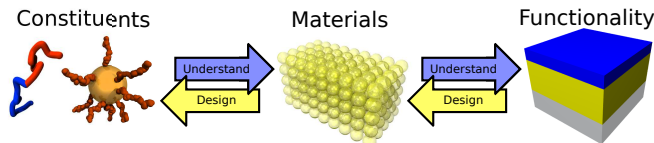
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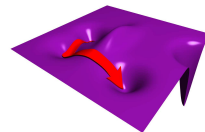
## A. Science Case

Twenty-first-century materials science has moved beyond bulk materials, composites, and blends, to the development of multi-component assemblies, incorporating nanoscale subunits and functional macromolecules, which are arrived at through non-equilibrium assembly pathways. Synchrotron x-ray scattering is critical to identify and build upon the structure-function relationships. As the grand challenge of materials design moves from the science of *observation* to the science of *control*, x-ray scattering holds enormous untapped potential. Its promise will be realized when beamlines provide sophisticated capabilities for combinatorial materials science. Moving beyond simplistic high-throughput methods, the Complex Materials Scattering (CMS) beamline will address this future, providing new tools for driven non-equilibrium assembly and rational materials design.



The over-arching challenge in materials science is the rational design of new materials, where given the required characteristics, the material structure is predicted; and for that particular structure, we can design appropriate constituents and assembly processes. Achieving this goal requires detailed understanding of material assembly at multiple length-scales. The Complex Materials Scattering beamline will enhance the pace of exploration by screening materials more rapidly and intelligently. High-throughput techniques have been shown to allow discovery of previously hidden structures and patterns. As such, we anticipate entire new classes of materials may arise from such explorations. Perhaps more importantly, however, by mapping out complex parameter spaces, the CMS will provide fundamental scientific insights in material behavior and assembly processes, thereby paving the way for truly rational material design.

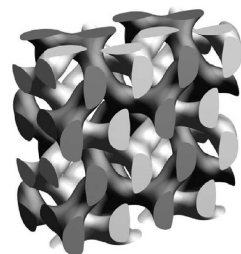
The vast majority of industrial materials are inherently non-equilibrium. For instance, most polymers are used in an amorphous or semicrystalline state, and most alloys are quenched into meta-stable states. Furthermore, it is now appreciated that for many materials, especially nano-materials, the final states are not just a matter of thermodynamic minima, but of kinetic barriers and path-dependent phenomena. In fact, non-equilibrium effects can be used productively, to select desired structures, since assembly processes can be strongly sensitive to external stimuli, such as applied fields or mechanical stress. In this regard, responding to the grand challenges of materials science means not just understanding the thermodynamic interactions, but engineering the potential energy landscape. All of these challenges can benefit greatly from the application of high-throughput techniques. The complexity inherent to hierarchical order, process-dependent phenomena, and multi-component systems, can all be addressed by high-speed, *efficient* exploration of parameter spaces.



The proposed beamline will enable the enormous community of soft-matter researchers, who rely on x-ray scattering, to continue to grow their programs to meet new materials challenges. With the transition from NSLS to NSLS-II, the substantial user base of existing beamlines X6B, X9, X10A, X10B, and X27C will be seeking access to versatile next-generation instruments: see Appendix, for Letters of Support showcasing the scientific impact. A complementary undulator proposal, Soft Matter Interfaces, will address the need for specialized interface studies. The CMS beamline aims to serve a broad community; without its construction, the diverse and high-impact science from these users would come to a halt. Moreover, BNL's Center for Functional Nanomaterials has programmatic objectives which go hand-in-hand with the science case presented here. This is evidenced by the CFN's formal investment into NSLS beamline X9, and continues with the participation of CFN scientific staff in the present proposal for NSLS-II.

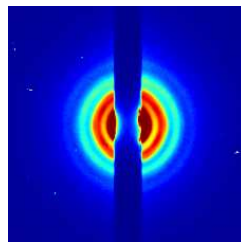
## Mesoporous Materials

Controlling structure and functionality in mesoporous thin films requires the optimization of a myriad of components and processing effects; the combinatorial capabilities of the CMS beamline will enable unprecedented progress. Mesoporous films have well-defined internal pores on the scale of 2 to 100 nm. Their high internal surface area makes them ideal for applications in separation membranes,<sup>1</sup> catalysis,<sup>2-4</sup> pollution control and CO<sub>2</sub> sequestering,<sup>5</sup> low-k dielectrics for microelectronics,<sup>6</sup> and sensors.<sup>7</sup> Conductive mesoporous materials, especially carbon and carbon composites, have been identified as high-performance energy materials for batteries, fuel cells, supercapacitors, and as three-dimensional electrode contacts in photovoltaics.<sup>8</sup> The double gyroid morphology in particular is attractive for many applications, but its stable formation can be challenging. In thin films defect formation and film shrinkage during processing limit application performance.



To fulfill the promise of mesoporous materials, it is critical to identify synthesis and processing conditions that result in the desired material properties. Conventional synthesis methods can produce materials with a wide range of different physicochemical properties dependent upon processing conditions. Moreover the structure in thin films and coatings are different from those found in the bulk, even if the processing conditions are the same. Thus, the fundamental processing-structure-property relationships in these materials are still poorly understood, especially in non-silica mesoporous materials. The CMS beamline will address these issues by enabling rapid study of material compositions, and by identifying the governing fundamental relationships. Mesoporous films are amenable to combinatorial gradients generated via flow coating,<sup>9</sup> which, combined with the small beam size of the CMS, will enable screening of the large parameter spaces. The variety of synthetic methodologies available in sol-gel processing naturally lends itself to combinatorial methods.<sup>10</sup> High throughput syntheses of sol-gel powders enabled the discovery of new mixed metal oxides for catalysis,<sup>11</sup> photoelectrochemical materials,<sup>12,13</sup> luminescent materials,<sup>14</sup> and thermoelectric materials.<sup>15</sup> The critical steps of non-equilibrium film formation and drying will be studied online, using realtime x-ray scattering measurements.

This competence in studying porous materials will have a significant impact in a variety of energy industries.<sup>16-19</sup> The petroleum refining industry has been utilizing mesoporous materials for decades in the form of zeolites for catalysis.<sup>2</sup> Similarly, the porosity of coals and mesostructure of shales remain areas of critical industrial significance. Lastly, the separator films used in battery technologies, particularly Li ion batteries for hybrid vehicles, are of mounting technological and social importance. This film prevents batteries from overheating and failing. The performance and degradation of these porous films are rooted in their complex nanostructure. The capabilities envisioned for the CMS will enable this nanostructure to be probed in detail, determining porosity and pore geometry, as well as identifying dominant failure mechanisms. The rapid access and high-throughput approach of the CMS will be used as a screening tool in determining the suitability of materials for energy and sustainability applications.



## Electrostatically-Assembled Materials

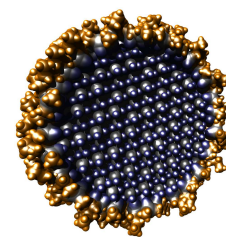
In ordered polyelectrolyte-surfactant complexes, assembly of even the simplest systems depends upon the proportions of amphiphile, polyelectrolyte, co-surfactant, water, oil, and salt, requiring a combinatorial approach when seeking to design materials with distinct phase morphologies. Understanding their phase behavior allows design of many industrial mixtures including cosmetic, health

products, and agricultural agents. Furthermore, these constituents assemble into meso-scale porous structures, which can be used as templates for solid nanoporous materials, using polymerization and cross-linking strategies. Potential areas of impact include the automotive industry’s need for temperature resistant fuel-cell membranes, the bioseparation industry’s need for better filters, and the pharmaceutical and cosmetic industries’ need for controlled drug delivery.<sup>20–23</sup>

The large number of individual components results in extremely complex phase diagrams. Once the components for a material with desired properties have been chosen, the challenge reduces to characterization as a function of composition. Small-angle x-ray scattering is ideally suited to identify phases in these well ordered emulsions, and research underway currently uses robotic sample preparation in standardized well plates, taken directly to the x-ray beamline. To explore this massive parameter space more effectively, the CMS beamline will be tailored to support the needs of combinatorial materials science, including specialized software, controls, and data handling. *CFN user research.*

## Nanoparticle Synthesis and Assembly

The challenging synthesis and assembly of nanoparticles would be revolutionized by an efficient exploration of the relevant compositional and processing parameter spaces. Nanoparticles have been identified as key components in a variety of applications: their small size gives them unique, often extraordinary, catalytic and optical properties. Currently, synthesis of monodisperse nanoparticles, with controlled surface properties, remains extremely challenging. Hybrid organic-inorganic copolymers offer a potential solution: the structural features of the parent block-copolymer dictate the structural features of the final metallic nanoparticles.<sup>24–26</sup> However the phase diagram is large and complex. X-ray scattering data can be used to monitor particle size, shape, and polydispersity, in addition to identifying the crystal polymorph. Using this data as feedback, and an *in-situ* microfluidic reactor, the CMS beamline will autonomously adjust reagent feeds in order to synthesize particles of a target size and composition. Thus, the CMS beamline will overcome the typical bottleneck in studies of synthesis by automating searches in large, multi-dimensional, parameter spaces. Operated in this mode, the Complex Materials Scattering beamline will become a highly efficient synthesis robot.<sup>27</sup>

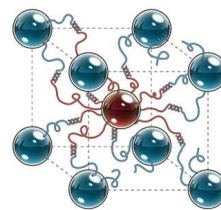


This approach is generic and can be applied to many problems, such as protein folding, protein crystallization, and pharmaceutical formulations. In particular, the study of nanoparticle assembly into superstructures and lattices,<sup>28,29</sup> necessary for a variety of demanding applications in nanotechnology, could be automated. Stochastic searches will enable discovery of superstructures and materials that a human would not have thought to design. There are undoubtedly many unique and high-performance materials hiding in unexplored portions of phase diagrams. Moreover, the structure of the parameter spaces themselves will provide key scientific insights into assembly processes. *CFN core research.*

## Bio-Programmable 3D Nanoparticle Assembly

The design of assemblies that will respond to externally applied stimuli is at the heart of bionanotechnology. The intrinsic plasticity of biomolecules, and their multi-minima energetic landscapes, contribute to their capability to be dynamically reconfigured on demand.<sup>30</sup> The further capacity for *programmed* responses is also within reach, by exploiting DNA hybridization. In recent advances, DNA motifs have been used to organize 3D structures for directing nano-objects into position,<sup>31–34</sup> and to induce structural switching on demand.<sup>35</sup> To fully realize the potential of these new assembly

methods, it is necessary to discover the extents and limitations of scaffold design.<sup>36</sup> The kinetic and energetic factors which control assembly and particle positioning must also be explored.<sup>37,38</sup> *In-situ*, time-resolved x-ray probes can detect subtle structural changes imposed by solution conditions and other environmental variables. X-ray scattering can monitor scaffold formation and measure the structure and binding kinetics, quantifying cooperative effects.<sup>39</sup>



The CMS beamline, envisioned to incorporate ancillary probes such as optical techniques, will enable the discovery of correlations between local molecular changes and organization of the extended system, which is critical for design to proceed. Arising from this research will be “smart” materials which respond, reconfigure, and react to external inputs, with site-selective binding that incorporates nanoparticles and other functional moieties. *CFN core research.*

## Smart Elastomers

Detailed structural studies of stimuli-responsive elastomers necessarily require an x-ray scattering beamline that can measure materials *during* perturbation. One of the unique properties of polymers is their viscoelasticity, a consequence of long-chain coiling and entanglement. A current challenge in polymer science and engineering is to fabricate “smart elastomers” that have responsive properties: for example, as a discontinuous change in the modulus, or adhesion upon the application of an external stimulus, such as a change in temperature, humidity, or illumination. These responsive properties enable the generation of self-healing polymers, which represent a breakthrough in protective coatings and structural components; and shape-memory polymers, which are useful as sensors and actuators in fields ranging from biomedicine to aerospace. A variety of promising smart elastomer systems have been identified, including block-copolymer architectures, side-chain crystalline polymers, and nanoparticles/polymer composites. The proposed modular design of the Complex Materials Scattering beamline will allow *in-situ* characterization of the morphological behavior of these materials under mechanical loading to understand the structure-property relationships in these systems. Time-resolved *in-situ* measurements will enable the precise mechanism of stimuli-responsive behavior to be uncovered.

## Polymer Crystallization

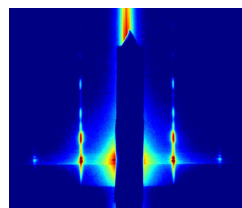
Polymer crystallization is a strongly non-equilibrium and path-dependent process; better understanding of the process can only arise through detailed *in-situ* study. Recently, large-period structures in polydisperse crystallizable block copolymers<sup>40</sup> have been identified as ideal systems for photonic materials operating at visible light wavelengths.<sup>41</sup> The crystallization of these systems is non-trivial, and demands structural measurements to very low  $q$ , ideally using a small x-ray beam in order to map structure and orientation across specimens, such as in fibers, spherulites, and molded articles. Importantly, the crystallization must be studied temporally, as a driven-assembly process.

The global market of polyolefins, especially polyethylene and polypropylene, exceeds 200 million tons, with 75% of polyethylene processed into films for packaging applications. It is therefore of continual interest to study the crystallization of these materials under shear flow. This can quantify how molecular structure and processing regulate the material’s mechanical and aesthetic properties. *In-situ* measurements are mandatory, since structural features at all length-scales evolve during processing and dictate the final material properties. Despite substantial industrial interest, the mechanisms of polymer crystallization are still poorly understood; technological processing remains largely empirical. This is mainly because semicrystalline polymers are in non-equilibrium states, with their formation strongly dependent on the temperature and mechanical processing

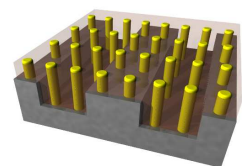
conditions. Progress in understanding these materials requires a versatile beamline that can rapidly quantify structure *in-situ* during processing. The CMS beamline will provide the versatility and performance necessary to address these critical non-equilibrium questions, in conjunction with sample environments which can simulate industrially-relevant processing operations: specifically extrusion, heating/cooling,<sup>42</sup> stretching,<sup>43</sup> fiber spinning, film blowing, tape extrusion, and reaction injection molding.

## Block-copolymer Assembly

Block-copolymers have emerged as a powerful tool for nanoscale control of material properties,<sup>44</sup> but progress is limited by a lack of detailed structural knowledge at multiple length-scales. Block-copolymers are the premiere soft materials for the self-assembly of periodic nanostructures with dimensions of 1 nm to 100 nm. Control of nanoscale order is crucial for a variety of emerging applications. For example, the length-scale of ordering in a block-copolymer can be precisely tuned to maximize the amount of active material in organic photovoltaics. In fuel cells, physically crosslinked block-copolymers can be used to localize ionic domains to enhance conductivities, and to limit swelling and dissolution to control mechanical properties. Applications in photonics are also important, since block-copolymers can form periodic structures commensurate with visible wavelengths. Despite active research, control and understanding of morphology remains the key challenge. The broad  $q$ -range x-ray scattering capabilities of the CMS beamline will elucidate the interplay between size-scales: molecular packing, nanoscale morphology, mesoscale ordering, and macroscopic properties.



The size and periodicity of block copolymer domains makes them attractive for applications in device patterning.<sup>45</sup> However, building next-generation electronics through self-assembly will require registration between polymer domains and substrate feature. These demands have motivated a great deal of research in the area of templated self-assembly, where topographic or chemical patterns on a substrate are used to direct the placement of block-copolymer domains.<sup>45–47</sup> Such methods hold the promise of combining the nanoscale control of self-assembly with the macroscopic registry of established lithography.<sup>48,49</sup> However to realize these applications requires simultaneous characterization of the nanostructure and the microstructure. The broad- $q$  capabilities of the CMS will be crucial for rapid and quantitative analysis of block copolymer domain shapes through the film thicknesses,<sup>50</sup> the wetting (or contact) of domains near the substrate interface,<sup>50</sup> orientational order, and long-range pattern quality.<sup>51</sup>



*CFN core research.*

## Organic Electronics and Photovoltaics

In order to realize the potential of organic materials for electronic applications, we must understand the interplay between molecular packing, domain structure, and device performance. Organic electronics are being studied as an alternative to conventional inorganic semiconductors.<sup>52–54</sup> Organic materials can be deposited through established printing methods and have the potential to dramatically reduce the manufacturing costs for applications from large-format displays and solid-state lighting, to solar power generation. The primary limitations to wide-scale use of organic electronics are performance and lifetime. However, most attempts to increase the material lifetime result in reduced performance. Understanding how molecular structure simultaneously dictates device lifetime and microstructure, which in turn determines performance, will greatly accelerate the development

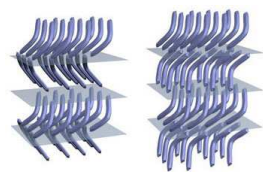


of technologically-successful materials.

Researchers currently use synchrotron-based x-ray diffraction to determine the crystal structure, orientation, size, and degree of crystallinity of functional thin films of organic electronic semiconductors. These parameters have been shown to be correlated with the electronic properties of the organic materials. The broad  $q$ -range of the CMS beamline will allow simultaneous measurements of molecular packing and domain structure. This is particularly important for multiple component systems, such as organic photovoltaics, where both the structure of the individual phases and their intermixing determine their performance. Furthermore, the microbeam capabilities of the beamline will enable structural mapping in these inherently heterogeneous systems. *CFN core research.*

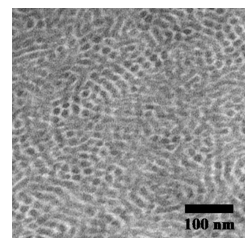
## Liquid Crystals with Complex Morphologies

New applications in liquid crystalline (LC) materials increasingly call for miniaturization and molecular confinement within the devices, making scrutiny of their structures on micron length-scales increasingly critical. Furthermore, micron-scale morphology is integrally related to function in this complex class of materials. For example, lyotropic chromonic liquid crystals (LCLCs)<sup>55,56</sup> find use as orienting and light-polarizing layers in flexible displays.<sup>57</sup> These materials have potential application as biosensors: highly specific antibody-antigen reactions generate microbial aggregates that can distort liquid crystal matrices, enabling optical detection of agents such as anthrax.<sup>58</sup> The self-assembly of LCLCs is greatly influenced by dopants.<sup>59,60</sup> Additives cause condensation of aggregates with nontrivial morphologies of phase separation, such as tactoids and toroids of the nematic and hexagonal columnar phase coexisting with the isotropic melt.<sup>61</sup> Pinpointing the ensuing orientational and positional ordering within individual domains, using a microfocused synchrotron x-ray beam, is a priority. Similar arguments apply to LC phases formed from reduced symmetry mesogens. In the processable fluid state, some of these LCs exhibit special properties, such as large electric polarization induced by mechanical flexure, potentially useful for small-scale green power generation. When polymerizing or crosslinking systems based on complex-shaped reactive LC monomers, nanoscale “seed” structures formed in the early stages are of particular importance. Unconventional combinations of long-range orientational and short-range positional ordering, and subtle variations of known phases, probably underlie their properties. Progress in novel LCs requires cutting-edge SAXS/WAXS performance as well as the *in-situ* application of external influences that directly couple to molecular orientation: magnetic fields, electric fields of variable frequency and magnitudes, and precisely-controlled mechanical stresses (specifically shear and curvature distortions) would be of enormous value.



## Nanostructured Materials

Nanomaterials hold tremendous promise but understanding them requires screening a massive number of compositional and processing combinations while characterizing order at all length-scales. Materials built from nanocomponents possessing unique mechanical, optical, electrical, or catalytic properties, can address the Grand Challenges emphasized in the DOE's report “Directing Matter and Energy”, such as designing materials with tailored functions, mastering energy on the nanoscale, and controlling matter away from equilibrium. Self-assembly<sup>62–64</sup> offers a tremendous cost and control advantages compared to lithographic methods. Furthermore, self-assembly addresses tasks that are intrinsically challenging for conventional lithography processes, such as creating three-dimensional architectures or



structures containing pre-fabricated functional nano-objects. Incorporating biomolecules into the design of nano-objects enables highly selective recognition between various components.<sup>64–66</sup> In order to enable rational fabrication of 3D structures from nano-components, a host of interactions and effects must be studied, including entropy, electrostatics, recognition and non-specific interactions,<sup>34,67</sup> and particle shape, symmetry and anisotropy.<sup>29</sup> The high-throughput capabilities of the CMS beamline will enable screening of the large parameter spaces inherent to multi-component nanomaterials. Online time-resolved probing of assembly will enable delicate parameter spaces to be explored intelligently, and in detail. Importantly, the CMS will enable direct *in-situ* probing of kinetic pathways for structure formation, including formation in response to external stimuli. The wide  $q$ -range will be invaluable for correlating nanoparticle super-structure with local organization of biomolecules. The beamline’s microfocusing and incorporation of micro-fluidic methods will be crucial for studying the kinetics of disorder-order transitions and structure development, while scanning SAXS can provide information about phase coexistence and dependence of structure on molecular/ionic gradients.

The broad capabilities of the CMS will also be exceptionally useful in studies of nanocomposites, including those containing plate-like fillers such as the well-studied clays or the more recently-developed graphene. In more conventional fiber-reinforced composites, in particular the semicrystalline isotactic polypropylene, the microbeam capabilities of the CMS will permit measurements of the structure as a function of distance from the fiber axis, to directly probe the fiber’s nucleating power<sup>68</sup> and the mechanism by which the crystal polymorph is selected.<sup>69</sup>

## B. Beamline Concept and Feasibility

**Measurement Modes:** The Complex Materials Scattering endstation will be a microbeam x-ray scattering instrument optimized for transmission-mode experiments, acquiring data across a wide  $q$ -range (simultaneous WAXS/SAXS/USAXS). The expected  $q$ -range, from  $0.0004 \text{ \AA}^{-1}$  to  $7.0 \text{ \AA}^{-1}$ , will enable probing size-scales from  $\approx 1 \text{ \AA}$  to  $\approx 1 \text{ }\mu\text{m}$ . Using available detectors, we anticipate pixel-limited  $q$ -resolution of  $0.002 \text{ \AA}^{-1}$  in the wide-angle regime and  $7 \times 10^{-5} \text{ \AA}^{-1}$  in the small-angle regime. Multi-axis translational and rotational positioning hardware will enable reciprocal-space mapping for oriented nanostructures. These multi-axis sample stages will be suitable for reflection-mode operation, thereby allowing grazing-incidence scattering (GIXD/GISAXS) experiments.

In order to enable high-throughput operation, large-area translation stages, designed to accept standardized well-plates, will be available. Additionally, a robotic sample changer will enable the instrument to operate autonomously and continuously, maximizing beam usage. We envision the hutch having a small interlocked chamber allowing users to transfer new samples into a sample queue inside the hutch. This capability will also facilitate the proposed ‘rapid access’ mode, where users can be allocated smaller blocks of beamtime more frequently.

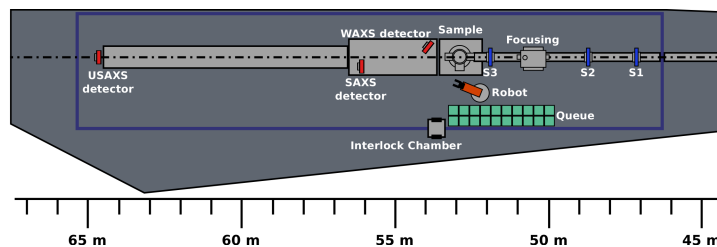
We have calculated that beam focusing down to  $\approx 20 \text{ }\mu\text{m}$  is feasible. This spot-size, combined with *in-situ* optical microscopy, will be crucial for mapping of heterogeneous materials and scanning combinatorial gradients. It will also be necessary for mapping inside microfluidic systems, where the spatial resolution is converted into time-resolution. This will enable kinetic measurements of liquid-phase mixing, reactions, and assembly. Computer-control of microfluidic chips will enable exploration of multi-dimensional parameter spaces without human intervention.

**Endstation Design:** We specify a three-pole wiggler source, energy tunability from 5 to 20 keV, and a multilayer monochromator (energy resolution 0.5%) in order to maximize flux for high-throughput measurements. The option to switch to a silicon crystal monochromator (energy reso-



lution 0.01%) for high-resolution measurements is anticipated. The calculated flux for our proposed configuration is roughly  $2 \times 10^{10}$  photons/s/0.01%bw at the sample position. This flux provides appropriate dynamic range for measurements on soft materials, and is sufficient to enable high-speed measurements on a wide variety of structured samples of scientific interest.

The CMS will require a hutch approximately 3 m wide by 20 m long. The first 7 m of evacuated flight-path will be used for motorized slits and optics, which will focus the beam onto the sample position. A 10 m evacuated flight-path after the sample will contain three area detectors, built onto motorized positioning stages. This enables access to the wide  $q$ -range necessary for hierarchical samples, and enables rapid switching between samples that may require different  $q$ -ranges. The detectors and acquisition systems will handle 30 Hz data collection (33 ms temporal resolution), allowing for kinetic measurements from strongly-scattering systems, and will be crucial to enabling real-space mapping of materials.



The sample chamber will be vacuum-compatible, in order to accommodate low-background measurements frequently necessary for soft materials. The chamber will be modular and removable, to accommodate a wide variety of user needs. In particular, we expect samples to be probed using a variety of stimuli: magnetic fields, electric fields, laser irradiation, thermal fields and gradients, and a general control of vapor composition and pressure.

**Feasibility:** The proposed science program requires good beam stability, moderate microfocusing capabilities, and simultaneous access to a wide  $q$ -range. A three-pole wiggler source at NSLS-II can provide the flux, energy range, and beam quality necessary to achieve this scientific mission. The CMS will take advantage of the beam stability at NSLS-II, which will be crucial for making quantitative cross-comparisons across many samples (or positions within a sample). The Center for Functional Nanomaterials (Brookhaven National Laboratory) will maintain its commitment to x-ray scattering methods by supporting the CMS beamline. Transitioning CFN equipment from the X9 beamline at NSLS will help with construction.

## C. Required Technical Advances

The CMS endstation will require advances in software, automation, and integration. Robotic solutions for handling delicate user samples (capillaries, thin films on wafers, etc.) will need to be designed. A sample chamber capable of automated evacuation and opening/closing will be required to allow access to the sample-changing robot. In order for the beamline to operate continually on a dynamically-adjusted sample queue, a means for inserting new samples into the protected x-ray hutch will be required. Currently we envision a small interlocked chamber, with the sample-changing robot transferring samples from the chamber to the queue holding area. The main challenges are x-ray beam containment safety considerations.

Although all beamlines require a robust and complex software stack for operation, the CMS will require specialized software development. A suite of efficient analysis tools will be required to deal with the large volume of data. Control software for the robotics will need to be

adapted. In addition to simple queuing and scripting, the beamline will require software that can respond dynamically to the results of measurements. This decision/control software, which will enable efficient utilization of the beamtime, will require advanced programming methods, including techniques from artificial intelligence and machine learning. The wide variety of algorithms that have been developed for data fitting and physics modeling will need to be adapted to enable the CMS to explore physical parameter spaces. The required software solutions are all feasible given modern programming paradigms and computer capabilities. However, they will require staff with programming expertise beyond what is required for a conventional beamline.

The technical challenges involved in building the CMS beamline are surmountable. Existing technologies and expertise (e.g. from protein crystallography beamlines) can be leveraged to create what will be a beamline with unique capabilities. The technical developments (especially software) will be easily exported to other x-ray endstations and synchrotron facilities.

## D. User Community and Demands

Complex materials by their nature are multicomponent systems arranged in a structural hierarchy, and their study requires making the most of multi-dimensional data sets. Large swaths of sample component space are surveyed, with structural measurements over many orders of magnitude in real and reciprocal space. The pioneers of these techniques have historically been very active in developing synchrotron beamlines for small- and wide-angle scattering. Over the years, facilities such as NSLS Beamline X27C and ESRF Beamline ID13 have laid the groundwork for the high-throughput methods envisioned here.

The impact is seen worldwide as thousands of users in Soft Matter utilize SAXS/WAXS stations. These experimenters develop huge suites of ancillary capabilities: mechanical rigs, environmental chambers, *in-situ* optical microscopy, and batch data analysis methods. The majority of these designs are shared across the community to the benefit of all. Closer to home, we maintain a list of over 200 key NSLS-I users, who support a constellation of collaborative scientists, not themselves scattering experts. These users demand x-ray beams with hundred- or ten-micron spatial resolution. The full range of reciprocal space is required. If long working distances and fast detectors are provided, these users will develop sample manipulation capabilities to new heights.

Hundreds of experiments will be represented by this core SAXS/WAXS community as our proposed CMS beamline at NSLS-II takes on the role played currently by several NSLS-I beamlines. Frontier researchers in complex materials also pave the way for specialized NSLS-II developments, such as coherent x-ray applications. Our community has a perennial presence in synchrotron workshops, on Scientific Advisory Committees, and in the commissioning of new facilities. The authors of the present proposal have convened several well-attended NSLS-II development workshops. Refer to the appendix for Letters of Support, which provide a view of the breadth and depth of the user community.

The Center for Functional Nanomaterials (CFN, Brookhaven National Lab) actively develops x-ray scattering methods for study of nanosystems. In contributing equipment, funding, and staff time to the X9 beamline at NSLS, the CFN has allowed a greater nanomaterials community, to use the powerful capabilities of the synchrotron. The CFN aims to continue this highly successful venture by supporting the development of the CMS beamline at NSLS-II. The CFN's diverse and productive user community will thus contribute to the high-impact science of the CMS.

## E. Proposal Team Expertise and Experience

**Kevin Cavicchi:** 12 yrs experience in synthesis and characterization of novel polymers and self-assembly. Experienced GISAXS user for ordered block copolymer films (NSLS and APS).

**Christian Burger:** 22 yrs of experience in synchrotron SAXS and WAXS of soft matter: polymers, biopolymers, block copolymers, composites, fibers, polyelectrolyte-surfactant complexes.

**Elaine DiMasi:** 14 yrs experience, LSS design at NSLS and APS, 60+ publications. Novel scattering studies of biomineralization and templating at mineral-organic interfaces.

**Andrei Fluerașu:** Over 10 yrs of synchrotron experience, group leader of the NSLS-II coherent hard x-ray beamline. Interests include XPCS studies of dynamics; developed microfluidic-XPCS.

**Seth Fraden:** 30 yrs research experience in soft condensed matter, biological liquid crystals, colloids, protein crystallization, microfluidics, and light scattering.

**Masafumi Fukuto:** 15 yrs of experience, including liquid-interface diffuse scattering, surface critical and fluctuation phenomena, biomolecular and nanoparticle assembly at liquid interfaces.

**Oleg Gang:** 15 yrs of experience, applied scattering methods to study phase transitions at interfaces, wetting on nanostructured surfaces, self-assembly in nanoscale systems, discovered 3D ordering in DNA-guided nanoparticle assemblies.

**Benjamin S. Hsiao:** Chair, Stony Brook University Chemistry Department and X27C Spokesperson. Pioneered studies of structure, morphology, and processing relationships in polymers.

**R. Joseph Kline:** 10 yrs of experience, including grazing-incidence diffraction and small-angle scattering studies of organic electronic and photovoltaic materials. Member of SSRL UEC.

**Satyendra Kumar:** 34 yrs experience in studies of structure and phase transitions in liquid crystals using x-ray and neutron scattering, reflectivity, heat-capacity, and electro-optical techniques.

**Oleg Lavrentovich:** 28 yrs of soft matter research, coauthored a textbook “Soft Matter Physics: An Introduction” (with M. Kleman), pioneered 3D optical microscopy of liquid crystals.

**Benjamin Ocko:** 25 yrs of experience, pioneered studies of electrode surfaces and liquid interfaces, discovered surface freezing. Developed *in-situ* GISAXS techniques. Designed & built X22A&B and 9ID (APS).

**Ron Pindak:** Over 30 yrs experience in synchrotron research. Co-pioneered the use of synchrotron x-ray diffraction to study 2D physics in liquid crystals and resonant scattering to measure molecular orientational ordering. Experienced in implementing bend-magnet micro-beam diffraction.

**Miriam Rafailovich:** 30 yrs experience and 350+ publications in x-ray scattering, soft condensed matter, tissue engineering, and polymer physics research.

**Richard Register:** 25 yrs experience at synchrotrons. Co-invented block copolymer nanolithography; broad expertise from synthesis to structural characterization to property optimization.

**Samuel Sprunt:** 25 yrs experience in liquid crystals and soft matter research. Pioneer development of nanosecond photon correlation spectroscopy, applied to freestanding liquid crystal films.

**Helmut H. Strey:** 15 yrs of experience, scattering methods to study self-assembled biopolymers. Discovered line-hexatic phase in DNA. Won APS Dillon medal in 2003. Developed combinatorial materials x-ray scattering beamline at NSLS.

**Bryan D. Vogt:** 24 publications using national scattering facilities, 2008 NSF CAREER awardee, developed x-ray based technique for ultrabroadband characterization for flexible electronics.

**Wen-Li Wu:** 30 yrs of experiences in x-ray and neutron scattering, pioneered x-ray scattering and reflectivity for nano-pattern characterization.

**Lutz Wiegart:** Research experience in structure and dynamics of soft matter systems. Assistant Physicist responsible for construction of the coherent hard x-ray scattering beamline at NSLSII.

**Kevin Yager:** 10 yrs experience with neutron and x-ray techniques for studies of soft materials. Developed SANS methods for mapping reciprocal space. Co-managing X9 beamline at NSLS.

## F. Suggestions for BAT Membership

The following scientists have been identified as capable and willing to serve on the Beamline Advisory Team:

1. **Kevin Yager** (Proposal Spokesperson), Assistant Materials Scientist, Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973. 631-344-7608. kyager@bnl.gov
2. **Elaine DiMasi**, Scientist, National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY 11973. 631-344-2211. dimasi@bnl.gov
3. **Oleg Gang**, Scientist, Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973. 631-344-3645. ogang@bnl.gov
4. **Benjamin S. Hsiao**, Professor, Department of Chemistry, Stony Brook University, Stony Brook, NY 11794. 631-632-7793. bhsiao@notes.cc.sunysb.edu
5. **Alexander Norman**, Senior Scientist, ExxonMobil Research and Engineering, Annandale, NJ 08801. 908-730-2571. alexander.norman@exxonmobil.com
6. **Benjamin Ocko**, Scientist, Condensed Matter Physics & Materials Science, Brookhaven National Laboratory, Upton, NY 11973. 631-344-4299. ocko@bnl.gov
7. **Ron Pindak**, Scientist, National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY 11973. 631-344-7529. pindak@bnl.gov
8. **Helmut H. Strey**, Associate Professor, Biomedical Engineering, Stony Brook University, Stony Brook, NY 11794. 631-632-1957. Helmut.Strey@stonybrook.edu
9. **Randall E. Winans**, Scientist, Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439. 630-252-7479. rewinans@anl.gov
10. **Wen-Li Wu**, NIST Fellow, Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD 20899. 301-975-6839. wen-li.wu@nist.gov

## References

- [1] Yunfeng Lu, Rahul Ganguli, Celeste A. Drewien, Mark T. Anderson, C. Jeffrey Brinker, Weiliang Gong, Yongxing Guo, Hermes Soye, Bruce Dunn, Michael H. Huang, and Jeffrey I. Zink. Continuous formation of supported cubic and hexagonal mesoporous films by sol-gel dip-coating. *Nature*, 389 (1997) 364–368.
- [2] Avelino Corma. From microporous to mesoporous molecular sieve materials and their use in catalysis. *Chemical Reviews*, 97 (1997) 2373–2420.
- [3] Dirk E. De Vos, Mieke Dams, Bert F. Sels, and Pierre A. Jacobs. Ordered mesoporous and microporous molecular sieves functionalized with transition metal complexes as catalysts for selective organic transformations. *Chemical Reviews*, 102 (2002) 3615–3640.
- [4] Daniel Brunel. Functionalized micelle-templated silicas (MTS) and their use as catalysts for fine chemicals. *Microporous and Mesoporous Materials*, 27 (1999) 329–344.
- [5] X. Feng, G. E. Fryxell, L.-Q. Wang, A. Y. Kim, J. Liu, and K. M. Kemner. Functionalized monolayers on ordered mesoporous supports. *Science*, 276 (1997) 923–926.
- [6] Shu Yang, Peter A. Mirau, Chien-Shing Pai, Omkaram Nalamasu, Elsa Reichmanis, Eric K. Lin, Hae-Jeong Lee, David W. Gidley, and Jianing Sun. Molecular templating of nanoporous ultralow dielectric constant (1.5) organosilicates by tailoring the microphase separation of triblock copolymers. *Chemistry of Materials*, 13 (2001) 2762–2764.
- [7] Hongyou Fan, Yunfeng Lu, Aaron Stump, Scott T. Reed, Tom Baer, Randy Schunk, Victor Perez-Luna, Gabriel P. Lopez, and C. Jeffrey Brinker. Rapid prototyping of patterned functional nanostructures. *Nature*, 405 (2000) 56–60.
- [8] Christophe J. Barb, Francine Arendse, Pascal Comte, Marie Jirousek, Frank Lenzmann, Valery Shklover, and Michael Grtzel. Nanocrystalline titanium oxide electrodes for photovoltaic applications. *Journal of the American Ceramic Society*, 80 (1997) 3157–3171.
- [9] Christopher M. Stafford, Kristen E. Roskov, Thomas H. Epps, and Michael J. Fasolka. Generating thickness gradients of thin polymer films via flow coating. *Review of Scientific Instruments*, 77 (2006) 023908.
- [10] Gerald Frenzer and Wilhelm F. Maier. Amorphous porous mixed oxides: Sol-Gel ways to a highly versatile class of materials and catalysts. *Annual Review of Materials Research*, 36 (2006) 281–331.
- [11] Sophie Biz and Mario L. Occelli. Synthesis and characterization of mesostructured materials. *Catalysis Reviews: Science and Engineering*, 40 (1998) 329.
- [12] Anders Hagfeldt and Michael Graetzel. Molecular photovoltaics. *Accounts of Chemical Research*, 33 (2000) 269–277.
- [13] Thomas F. Jaramillo, Sung-Hyeon Baeck, Alan Kleiman-Shwarsstein, and Eric W. McFarland. Combinatorial electrochemical synthesis and screening of mesoporous ZnO for photocatalysis. *Macromolecular Rapid Communications*, 25 (2004) 297–301.
- [14] Kurt D. Benkstein, Joseph T. Hupp, and Charlotte L. Stern. Luminescent mesoporous molecular materials based on neutral tetrametallic rectangles<sup>13</sup>. *Angewandte Chemie International Edition*, 39 (2000) 2891–2893.
- [15] Hugh W. Hillhouse and Mark T. Tuominen. Modeling the thermoelectric transport properties of nanowires embedded in oriented microporous and mesoporous films. *Microporous and Mesoporous Materials*, 47 (2001) 39–50.
- [16] Mark E. Davis. Ordered porous materials for emerging applications. *Nature*, 417 (2002) 813–821.
- [17] Jeffrey S Beck and James C Vartuli. Recent advances in the synthesis, characterization and applications of mesoporous molecular sieves. *Current Opinion in Solid State and Materials Science*, 1 (1996) 76–87.

- [18] Ulrike Ciesla and Ferdi Schth. Ordered mesoporous materials. *Microporous and Mesoporous Materials*, 27 (1999) 131–149.
- [19] C. Jeffrey Brinker, Yunfeng Lu, Alan Sellinger, and Hongyou Fan. Evaporation-Induced Self-Assembly: nanostructures made easy. *Advanced Materials*, 11 (1999) 579–585.
- [20] Robert van Reis and Andrew Zydney. Membrane separations in biotechnology. *Current Opinion in Biotechnology*, 12 (2001) 208–211.
- [21] Brian C. H. Steele and Angelika Heinzl. Materials for fuel-cell technologies. *Nature*, 414 (2001) 345–352.
- [22] R Langer. New methods of drug delivery. *Science*, 249 (1990) 1527–1533.
- [23] Meyer Rosen. *Delivery System Handbook for Personal Care and Cosmetic Products: Technology, Applications and Formulations*. William Andrew, January 2006.
- [24] Liliana A. Minea, Laura B. Sessions, Kjell D. Ericson, David S. Glueck, and Robert B. Grubbs. PhenylethynylstyreneCobalt carbonyl block copolymer composites. *Macromolecules*, 37 (2004) 8967–8972.
- [25] Laura B. Sessions, Liliana A. Minea, Kjell D. Ericson, David S. Glueck, and Robert B. Grubbs. Alkyne-Functional homopolymers and block copolymers through Nitroxide-Mediated free radical polymerization of 4-(Phenylethynyl)styrene. *Macromolecules*, 38 (2005) 2116–2121.
- [26] Robert B. Grubbs. Hybrid metal-polymer composites from functional block copolymers. *Journal of Polymer Science Part A: Polymer Chemistry*, 43 (2005) 4323–4336.
- [27] Emory M. Chan, Chenxu Xu, Alvin W. Mao, Gang Han, Jonathan S. Owen, Bruce E. Cohen, and Delia J. Milliron. Reproducible, High-Throughput synthesis of colloidal nanocrystals for optimization in multidimensional parameter space. *Nano Letters*, 10 (2010) 1874–1885.
- [28] Shelley A. Claridge, A. W. Castleman, Shiv N. Khanna, Christopher B. Murray, Ayusman Sen, and Paul S. Weiss. Cluster-Assembled materials. *ACS Nano*, 3 (2009) 244–255.
- [29] Mathew M. Maye, Dmytro Nykypanchuk, Marine Cuisinier, Daniel van der Lelie, and Oleg Gang. Stepwise surface encoding for high-throughput assembly of nanoclusters. *Nat Mater*, 8 (2009) 388–391.
- [30] Hao Yan, Xiaoping Zhang, Zhiyong Shen, and Nadrian C. Seeman. A robust DNA mechanical device controlled by hybridization topology. *Nature*, 415 (2002) 62–65.
- [31] Hao Yan, Sung Ha Park, Gleb Finkelstein, John H. Reif, and Thomas H. LaBean. DNA-Templated Self-Assembly of protein arrays and highly conductive nanowires. *Science*, 301 (2003) 1882–1884.
- [32] John D. Le, Yariv Pinto, Nadrian C. Seeman, Karin Musier-Forsyth, T. Andrew Taton, and Richard A. Kiehl. DNA-Templated Self-Assembly of metallic nanocomponent arrays on a surface. *Nano Letters*, 4 (2004) 2343–2347.
- [33] Dmytro Nykypanchuk, Mathew M. Maye, Daniel van der Lelie, and Oleg Gang. DNA-guided crystallization of colloidal nanoparticles. *Nature*, 451 (2008) 549–552.
- [34] Huiming Xiong, Daniel van der Lelie, and Oleg Gang. Phase behavior of nanoparticles assembled by DNA linkers. *Physical Review Letters*, 102 (2009) 015504.
- [35] Mathew M. Maye, Mudalige Thilak Kumara, Dmytro Nykypanchuk, William B. Sherman, and Oleg Gang. Switching binary states of nanoparticle superlattices and dimer clusters by DNA strands. *Nat Nano*, 5 (2010) 116–120.
- [36] Paul W. K. Rothmund. Folding DNA to create nanoscale shapes and patterns. *Nature*, 440 (2006) 297–302.
- [37] Mudalige Thilak Kumara, Dmytro Nykypanchuk, and William B. Sherman. Assembly pathway analysis of DNA nanostructures and the construction of parallel motifs. *Nano Letters*, 8 (2008) 1971–1977.
- [38] Oleg Gang and Daniel van der Lelie. Arbitrary assembly of nano-objects into 1D and 2D arrays, provisional patent application, January 2010.



- [39] Mathew M. Maye, Dmytro Nykypanchuk, Daniel van der Lelie, and Oleg Gang. A simple method for kinetic control of DNA-Induced nanoparticle assembly. *Journal of the American Chemical Society*, 128 (2006) 14020–14021.
- [40] Sheng Li, Richard A. Register, Brian G. Landes, Phillip D. Hustad, and Jeffrey D. Weinhold. Crystallization in ordered polydisperse polyolefin diblock copolymers. *Macromolecules*, 43 (2010) 4761–4770.
- [41] Phillip D. Hustad, Gary R. Marchand, Eddy I. Garcia-Meitin, Patricia L. Roberts, and Jeffrey D. Weinhold. Photonic polyethylene from Self-Assembled mesophases of polydisperse olefin block copolymers. *Macromolecules*, 42 (2009) 3788–3794.
- [42] Yueh-Lin Loo, Richard A. Register, Anthony J. Ryan, and Gregory T. Dee. Polymer crystallization confined in one, two, or three dimensions. *Macromolecules*, 34 (2001) 8968–8977.
- [43] Robert C. Scogna and Richard A. Register. Plastic deformation of ethylene/methacrylic acid copolymers and ionomers. *Journal of Polymer Science Part B: Polymer Physics*, 47 (2009) 1588–1598.
- [44] Michael J Fasolka and Anne M Mayes. Block copolymer thin films: Physics and applications. *Annual Review of Materials Research*, 31 (2001) 323–355.
- [45] Joona Bang, Unyong Jeong, Du Yeol Ryu, Thomas P. Russell, and Craig J. Hawker. Block copolymer nanolithography: Translation of molecular level control to nanoscale patterns. *Advanced Materials*, 21 (2009) 4769–4792.
- [46] Sang Ouk Kim, Harun H. Solak, Mark P. Stoykovich, Nicola J. Ferrier, Juan J. de Pablo, and Paul F. Nealey. Epitaxial self-assembly of block copolymers on lithographically defined nanopatterned substrates. *Nature*, 424 (2003) 411–414.
- [47] Ion Bitá, Joel K. W. Yang, Yeon Sik Jung, Caroline A. Ross, Edwin L. Thomas, and Karl K. Berggren. Graphoepitaxy of Self-Assembled block copolymers on Two-Dimensional periodic patterned templates. *Science*, 321 (2008) 939–943.
- [48] Andrew P. Marencic and Richard A. Register. Controlling order in block copolymer thin films for nanopatterning applications. *Annual Review of Chemical and Biomolecular Engineering*, 1 (2010) 277–297.
- [49] I.W. Hamley. Ordering in thin films of block copolymers: Fundamentals to potential applications. *Progress in Polymer Science*, 34 (2009) 1161–1210.
- [50] Erik W. Edwards, Marcus Mller, Mark P. Stoykovich, Harun H. Solak, Juan J. de Pablo, and Paul F. Nealey. Dimensions and shapes of block copolymer domains assembled on lithographically defined chemically patterned substrates. *Macromolecules*, 40 (2007) 90–96.
- [51] G. E. Stein, E. J. Kramer, X. Li, and J. Wang. Single-Crystal diffraction from Two-Dimensional block copolymer arrays. *Physical Review Letters*, 98 (2007) 086101.
- [52] Gilles Dennler, Markus C. Scharber, and Christoph J. Brabec. Polymer-Fullerene Bulk-Heterojunction solar cells. *Advanced Materials*, 21 (2009) 1323–1338.
- [53] Ana Claudia Arias, J. Devin MacKenzie, Iain McCulloch, Jonathan Rivnay, and Alberto Salleo. Materials and applications for large area electronics: Solution-Based approaches. *Chemical Reviews*, 110 (2010) 3–24.
- [54] Iain McCulloch, Martin Heeney, Michael L. Chabinyc, Dean DeLongchamp, R. Joseph Kline, Michael Cile, Warren Duffy, Daniel Fischer, David Gundlach, Behrang Hamadani, Rick Hamilton, Lee Richter, Alberto Salleo, Maxim Shkunov, David Sparrowe, Steven Tierney, and Weimin Zhang. Semiconducting thienothiophene copolymers: Design, synthesis, morphology, and performance in Thin-Film organic transistors. *Advanced Materials*, 21 (2009) 1091–1109.
- [55] J Lydon. Chromonic liquid crystal phases. *Current Opinion in Colloid & Interface Science*, 3 (1998) 458–466.
- [56] John Lydon. Chromonic mesophases. *Current Opinion in Colloid & Interface Science*, 8 (2004) 480–490.

- [57] T. Sergan, T. Schneider, J. Kelly, and O.D. Lavrentovich. Polarizing-alignment layers for twisted nematic cells. *Liquid Crystals*, 27 (2000) 567–572.
- [58] S. V. Shiyanovskii, T. Schneider, I. I. Smalyukh, T. Ishikawa, G. D. Niehaus, K. J. Doane, C. J. Woolverton, and O. D. Lavrentovich. Real-time microbe detection based on director distortions around growing immune complexes in lyotropic chromonic liquid crystals. *Physical Review E*, 71 (2005) 020702.
- [59] Andrei F. Kostko, Bani H. Cipriano, Olga A. Pinchuk, Lior Ziserman, Mikhail A. Anisimov, Dganit Danino, and Srinivasa R. Raghavan. Salt effects on the phase behavior, structure, and rheology of chromonic liquid crystals. *The Journal of Physical Chemistry B*, 109 (2005) 19126–19133.
- [60] Heung-Shik Park, Shin-Woong Kang, Luana Tortora, Yuriy Nastishin, Daniele Finotello, Satyendra Kumar, and Oleg D. Lavrentovich. Self-Assembly of lyotropic chromonic liquid crystal sunset yellow and effects of ionic additives. *The Journal of Physical Chemistry B*, 112 (2008) 16307–16319.
- [61] Lei Wu, Jyotsana Lal, Karen A. Simon, Erik A. Burton, and Yan-Yeung Luk. Nonamphiphilic assembly in water: Polymorphic nature, thread structure, and thermodynamic incompatibility. *Journal of the American Chemical Society*, 131 (2009) 7430–7443.
- [62] Palaniappan Arumugam, Hao Xu, Sudhanshu Srivastava, and Vincent M Rotello. Bricks and mortar nanoparticle self-assembly using polymers. *Polymer International*, 56 461–466.
- [63] Hao Zhang, Erik W. Edwards, Dayang Wang, and Helmuth Mohwald. Directing the self-assembly of nanocrystals beyond colloidal crystallization. *Physical Chemistry Chemical Physics*, 8 (2006) 3288–3299.
- [64] Lyndsey M. Greig and Douglas Philp. Applying biological principles to the assembly and selection of synthetic superstructures. *Chemical Society Reviews*, 30 (2001) 287–302.
- [65] Jim A. Thomas. Locking self-assembly: strategies and outcomes. *Chemical Society Reviews*, 36 (2007) 856–868.
- [66] Alexei V. Tkachenko. Morphological diversity of DNA-Colloidal Self-Assembly. *Physical Review Letters*, 89 (2002) 148303.
- [67] Huiming Xiong, Daniel van der Lelie, and Oleg Gang. DNA Linker-Mediated crystallization of nanocolloids. *Journal of the American Chemical Society*, 130 (2008) 2442–2443.
- [68] D. M. Dean, L. Rebenfeld, R. A. Register, and B. S. Hsiao. Matrix molecular orientation in fiber-reinforced polypropylene composites. *Journal of Materials Science*, 33 (1998) 4797–4812.
- [69] David M. Dean and Richard A. Register. Oriented gamma-isotactic polypropylene crystallized at atmospheric pressure. *Journal of Polymer Science Part B: Polymer Physics*, 36 (1998) 2821–2827.

## Appendix: Biographies

The attached biographical pages provide information about the experience and expertise of the proposal development team members.

1. Christian Burger, Scientist, Chemistry, Stony Brook University
2. Kevin Cavicchi, Assistant Professor, Polymer Engineering, University of Akron
3. Elaine DiMasi, Physicist, NSLS, Brookhaven National Laboratory
4. Andrei Fluerașu, Scientist, NSLS-II, Brookhaven National Laboratory
5. Seth Fraden, Professor, Physics, Brandeis University
6. Masa Fukuto, Associate Physicist, CMPMSD, Brookhaven National Laboratory
7. Oleg Gang, Scientist, CFN, Brookhaven National Laboratory
8. Benjamin S. Hsiao, Professor, Chemistry, Stony Brook University
9. R. Joseph Kline, Materials Research Engineer, Polymers Division, National Institute of Standard and Technology
10. Satyendra Kumar, Professor, Physics, Kent State University
11. Oleg Lavrentovich, Professor, LC Institute and Chemical Physics Program, Kent State University
12. Benjamin Ocko, Physicist, CMPMSD, Brookhaven National Laboratory
13. Ron Pindak, Scientist, National Synchrotron Light Source, Brookhaven National Laboratory
14. Miriam Rafailovich, Professor, Materials Science and Engineering, Stony Brook University
15. Richard A. Register, Professor, Chemical Engineering, Princeton University
16. Samuel Sprunt, Professor, Physics, Kent State University
17. Helmut H. Strey, Biomedical Engineering, Stony Brook University
18. Bryan D. Vogt, Assistant Professor, Chemical Engineering, Arizona State University
19. Wen-Li Wu, Fellow, Polymers Division, National Institute of Standard and Technology
20. Lutz Wiegart, Scientist, NSLS-II, Brookhaven National Laboratory
21. Kevin G. Yager (Spokesperson), Assistant Scientist, CFN, Brookhaven National Laboratory

## Appendix: Letters of Support

The attached letters of support provide a sampling of the diverse science and significant engagement of the soft and complex materials communities.

1. Harald Ade, Professor of Physics, North Carolina State University
2. Paschalis Alexandridis, UB Distinguished Professor, SUNY-Buffalo
3. Rama Bansil, Professor of Physics, Boston University
4. Surita Bhatia, Associate Professor, University of Massachusetts
5. J. Kent Blasie, Professor in Natural Sciences, University of Pennsylvania
6. R.M. Briber, Professor and Chair, University of Maryland
7. Stephen Z.D. Cheng, Dean, Coll. Poly. Sci. & Poly. Eng., University of Akron
8. Gilles Dennler, Dir. Device Research, Konarka Technology, Inc.
9. Ali Dhinojwala, Dept. Chair & Prof. Polymer Sci., University of Akron
10. Eric R. Dufresne, John J. Lee Asst. Professor, Yale University
11. Pulak Dutta, Professor, Physics & Astronomy, Northwestern University
12. Thomas H. Epps, III, Asst. Prof., Dept. Chem. Eng., University of Delaware
13. John Spencer Evans, Prof., Lab. for Chemical Phys., New York University
14. Mark D. Foster, Prof., Polymer Science, The University of Akron
15. David Gidalevitz, Asst. Prof. of Biophysics, Pritzker Institute
16. Helen Gleeson, Professor of Physics, The University of Manchester
17. Laurie Gower, Associate Professor, University of Florida
18. J.H. Harding, Professor of Materials Simulation, University of Sheffield
19. Alexander Hexemer, Physical Research Scientist, Lawrence Berkeley National Laboratory
20. Alamgir Karim, Goodyear Chair Professor, University of Akron
21. Doseok Kim, Prof., Dept. of Physics, Sogang University, Korea
22. David Kisailua, Assistant Professor, University of California, Riverside
23. Edgar E. Kooijman, Assistant Professor, Kent State University
24. Jeffrey B. Kortright, Staff Scientist, P.I., Lawrence Berkeley National Laboratory
25. Edward J. Kramer, Prof., Dept. of Materials Science, University California, Santa Barbara
26. Tonya Kuhl, Prof., Dept. Chem. Eng., University of California, Davis
27. Satyendra Kumar, Professor of Physics, Kent State University
28. Ioannia Kymissis, Asst. Prof., Electrical Eng., Columbia University
29. Jyotsana Lal, Biophysicist/Instrument Scientist, Argonne National Laboratory
30. Ka Yee Christina Lee, Prof, Dept. of Chemistry, The University of Chicago
31. R. Bruce Lennox, Chair, Dept. of Chemistry, McGill University
32. Christopher Li, Assoc. Prof. Mat. Sci. & Eng., Drexel University
33. Eric K. Lin, Chief, Polymers Division, National Institute of Standards and Technology
34. Laurence Lurio, Professor and Chair, Northern Illinois University
35. Olaf Magnussen, Professor Dr., University of Kiel
36. C.F. Majkrzak, Leader, Surface & Interfacial Sci., National Institute of Standards and Technology
37. Henry C. Margolis, Head, Dept. of Biomineralization, The Forsyth Institute
38. Hiroshi Matsui, Prof. & Chair, Dept. of Chemistry, CUNY-Hunter College
39. Sergiy Minko, Egon Maztijevec Chaired Prof., Clarkson University
40. Xiangyun Qiu, Research Fellow, National Institutes of Health
41. Jeffrey W. Ruberti, Associate Professor, Northeastern University
42. Thomas P. Russell, Dir., Energy Frontier Res. Ctr., University of Mass.
43. Jonathan V. Selinger, Prof. of Chemical Physics, Kent State University
44. Detlef-M. Smilgies, Sr. Research Associate II, CHESS
45. Nico A.J.M. Sommerdijk, Assoc. Prof., Mater. Chem., Technische Universiteit Eindhoven
46. Edwin L. (Ned) Thomas, Dept. Head, Mat. Sci. & Eng., Massachusetts Institute of Technology
47. Alexei Tkachenko, Material Scientist, Brookhaven National Laboratory
48. Alex Travesset, Prof. of Physics & Astronomy, Iowa State University
49. Andy H. Tsou, Section Head, Organic Materials, ExxonMobil
50. Richard A. Vaia, Technical Advisor, Air Force Research Laboratory